ELSEVIER
Available online at www.sciencedirect.com
SciVerse ScienceDirect
Physics Procedia 32 (2012) 464 – 469
Physics Procedia

18th International Vacuum Congress

Properties of the nonhydrogenous diamond-like carbon thin film on the 20CrNiMo surface by the hollow-cathode glow discharge

Fei Chen[a], Jiaqing Chen[b]*

[a]*Department of materials science and engineering, Beijing Institute of petrochemical technology, Beijing 102617, China*
[b]*Colloge of mechaniacl enginerring, Beijing Institute of petrochemical technology, Beijing 102617, China*

Abstract

Nonhydrogenous Diamond-like carbon (DLC) thin film was deposited on the surface of 20CrNiMo alloy by hollow cathode glow discharge technique. The high-purity graphite was selected as the cathode and Ar as the working gas. It is aimed to reduce the friction coefficient of the 20CrNiMo and to improve the property of the wear-resistance. The structure of the DLC thin film was analyzed by Laser Raman spectroscope. The surface morphology was observed through Atomic Force Microscope (AFM). The adhesion between the DLC thin film and the substrate was investigated with the scribe testing. The morphology of the scratch was observed by the Scanning Electron Microscope (SEM). The friction and wear behavior of the DLC thin film under dry sliding against GCr15 steel was evaluated on a ball-on-disc test rig. The results showed that it was feasible to prepare a DLC thin film of 0.6μm thickness by this experimental process. The surface roughness Ra was about 7~8nm. The DLC thin film has a good adhesion of critical load 52N. It has been found that the DLC thin film has excellent friction and wear-resistant behaviors. The friction coefficient of the 20CrNiMo substrate was about 0.50 under dry sliding against the steel, while the DLC thin film experienced much abated friction coefficient to 0.15 under the same testing condition.

PACS: 81.15.-z; 68.60.Bs
Keywords: DLC thin film; glow discharge; hollow-cathode; wear-resistance behavior

1. Introduction

Due to the comprehensive properties of high hardness, low friction coefficient and wear resistance, DLC thin film has become the hotspot that both domestic and international scholars study, which has great application perspective in mechanical sealing, knives, mould, precision instrument and optical parts [1~5].Commonly, DLC thin film has two categories, hydrogenous DLC and nonhydrogenous DLC. The former containing great amounts of H components of saturate sp3 bond is prepared mainly by CVD method, leading to the degradation of property due to hydrogen transgression. The sp3 bond in nonhydrogenous DLC is wholly composed of C atom, so it is more stable in structure. Compared with hydrogenous DLC, the counterpart has more similar or better properties in many

* Corresponding author. Tel.: +86-010-81292134; fax: +86-010-81292134.
E-mail address: chenfei@bipt.edu.cn.

 doi:10.1016/j.phpro.2012.03.586

aspects, such as the like electrical property, close or higher deposition rate and better adhesion and higher thermal stability with each kind of surface.

Nonhydrogenous DLC has many preparation methods, such as laser etching method, sputtering method, immediate ion beam (IB) method and filtering cathode arc (FCA) deposition method. Nonhydrogenous DLC has been widely used in so many aspects as magnetographic coating, reflection resistance coating with wear-resistance protection and infrared window, wear protection of bearing and sliding/friction parts and precision valves in automobile industry[6~9].

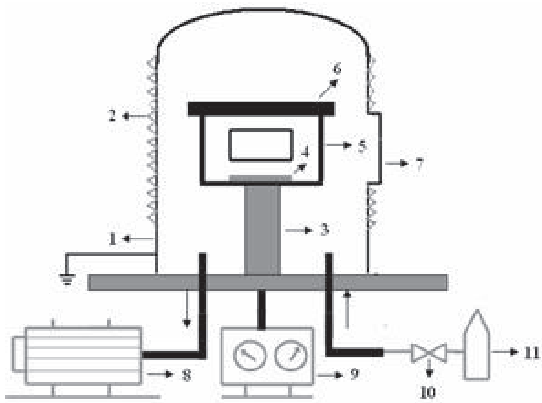
The article selects Ar with the purity of 99.99% as an auxiliary gas, the high pure graphite (99.99%) as the electrode, and uses hollow-cathode glow discharge effect to prepare nonhydrogenous DLC on the 20CrNiMo surface. The ultimate aim is to reduce the surface friction coefficient of the 20CrNiMo surface, enhance wear-resistance property and make prophase preparation for enabling the method to be used in metal sealing ring surface deposition DLC of the rolling bearing in future.

2. Experiment

2.1 Experimental method

Fig.1 is a schematic of experimental setup by hollow-cathode glow discharge preparation. After polishing, 20CrNiMo samples are put into acetone, alcohol and deionization water in turn to clean for 10～15min with ultrasonic wave, and then dried in the air and put into the hollow-cathode tube in vacuum chamber, the vertical distance between 20CrNiMo sample and graphite electrode is 30mm.

Draw the air pressure in vacuum chamber into 4Pa with mechanical pump, and then pour Ar gas into vacuum chamber to enable the vacuum degree to be 30Pa and exchange air for 5 minutes. After that, reduce Ar gas and enable the pressure in vacuum chamber to keep at 30Pa. Increase the voltage of direct current regulated power supply to 500V, bright glow appears in hollow-cathode tube, Ar is ionized into Ar ions, which bombard graphite electrode. The bombarded C ions in graphite electrode would deposit into DLC on the surface of 20CrNiMo sample under the reaction of plasma. The deposition lasts for 30 minutes. The deposition parameters of thin film are shown as Table 1.



1-Vacuum chamber 2-Cooling system 3-Bracket 4-Sample 5- Hollow-cathode tube 6- Graphite electrode 7-Quartz window 8- Mechanical pump 9-Direct current supply 10-Suspended body flowmeter 11-Ar gas supply

Fig.1 Schematic of experimental setup

Table 1 Deposition process parameters of thin film of nonhydrogenous DLC

Background air pressure/Pa	Working air pressure/Pa	Voltage/V	Current/A	Time/min
4	30	500	0.6	30

2.2 Test method

Make Raman spectra test for DLC thin film with RM2000 Laser Raman Spectrometer of British Reinshaw; make AFM appearance observation for DLC thin film with SPM9500-J3 Scanning Probe Microscope; the binding force between the thin film and the substrate is tested by MFT-4000 Multi-functional Material Surface Property Tester produced by Lanzhou Chemistry and Physics Research Institute of China Academy of Science, and make SEM observation for scratch with Japanese Shimadzu SSX-550 Scanning Electronic Microscope; test the friction property of samples under the circumstance of dry friction with MS-T3000 Ball-Plate Friction Wear Tester produced by Lanzhou Chemistry and Physics Research Institute of China Academy of Science; measure the film thickness with Times TR200 Surface Profiler.

3. Introduction

3.1 Raman analysis for DLC thin film

As shown in the Fig.2, Raman spectra of the prepared DLC thin film forms strong peak and extends towards lower wave numbers at 1580cm-1 or so, a shoulder peak takes shape nearly 1380cm-1, the DLC thin film structure reflected by the Raman spectra not only differs from the lamellar structure of graphite, but also from the tetrahedral structure of diamond, it is a kind of amorphous state (amorphous form) structure. The internal structure of DLC thin film with the very Raman spectra is: clusters with little sp2 are embedded in sp3 carbon bond network composed of olefin chain (C=C) and aromatic ring substitutes. Via Gauss fitting, Raman spectra is divided into D peak(1394cm-1) and G peak(1588cm-1), the ratio of the integral area of D peak and G peak is ID/IG=1.1; G peak represents the stretching vibration mode of C=C chain and C atom ring in sp2 clusters; while D peak only represents the vibration mode of C atom ring in sp2 clusters[10]. From the study of Ferrari[11] and Robertson[12], we can know G peak with high wave number in the Raman figure and higher ID/IG value show the order of thin film structure.

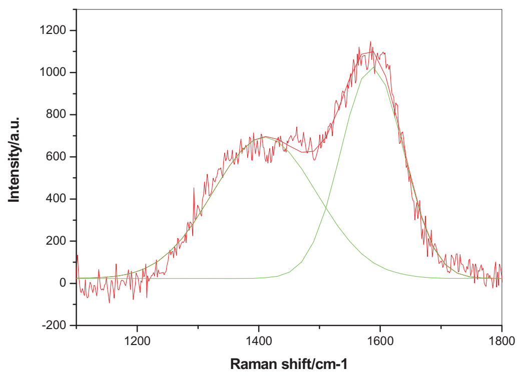


Fig.2 Raman spectra of DLC thin film

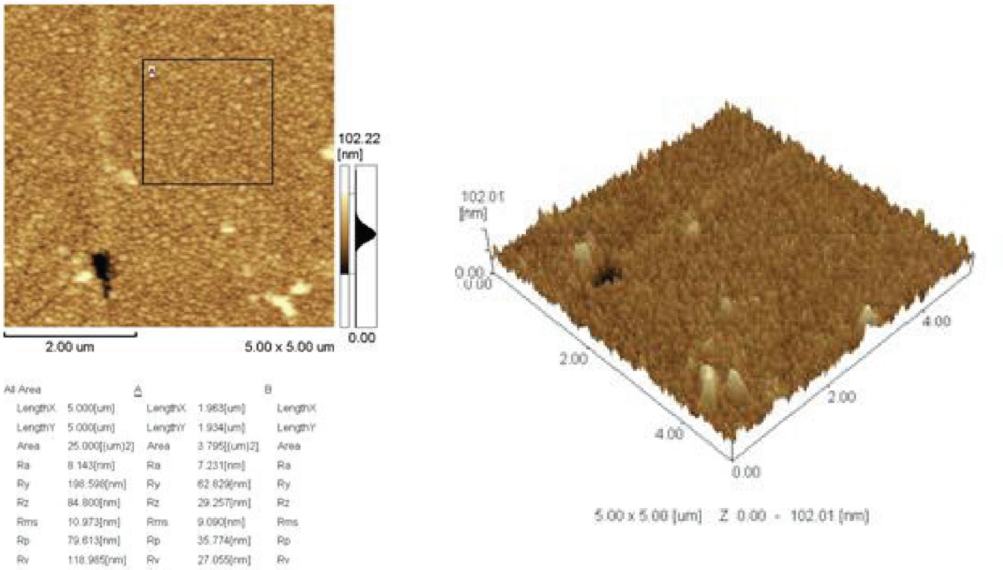
3.2 AFM analysis

Fig.3 shows the surface AFM appearance of DLC thin film prepared at the voltage of 500V, the current of 0.6A and working pressure of 30Pa. From Fig.3 (a), we can know thin film appears graininess, with more even grain diameter distribution; it is compact, without any obviously slim flaw. The surface roughness Ra is 7~8nm or so, higher than the one of DLC thin film prepared by other methods, which is mainly caused by the sputtering of Ar ions with high energy against the surface of deposited thin film. Surface profiler shows the depth of thin film is approximately 0.6μm. The good uniformity and compactness of thin film is closely associated with deposit methods, the ionized Ar ions repeatedly vibrate in hollow cathode and sharply increase energy, Ar ions with high energy bombard graphite electrode to generate C ions with certain kinetic energy and accelerate the migrating rate of C ions on the surface of thin film, enabling thin film to be compact and even, without any slim flaw.

From Fig.3 (b), we can know although the prepared DLC film is compact, there is also a little amount of island-appeared projections, we believe the projections may come from the cathodic graphite grains, the emitted graphite grains by the bombarding of Ar ions strike the substrate, some directly react, some adhere to the substrate to form film, as time goes on, graphite grains form based on the adhered grains.

3.3 Bonding force of DLC thin film and substrate

Use scratch instrument to measure the bonding force of DLC thin film and the substrate. Successively add the load into the scriber (diamond indenter) with automatic load machine, move the sample, sweep across the surface of the coating, get acoustic emission signal and friction alteration signal when the coating drops off with each sensor and the critical load of the bonding force of DLC thin film and the substrate [13]. Fig.4 is a SEM photograph of scratch of DLC thin film and Fig.5 is relationship between critical load and acoustic emission signal intensity. From the experiment, we know the critical load of the bonding force of DLC thin film and the substrate Lc=52N, showing the combination of the prepared DLC thin film and the substrate by hollow-cathode glow discharge is firm.



(a) 2 dimensional plane figure (b) 3 dimensional spatial figure

Fig.3 AFM morphology of DLC thin film

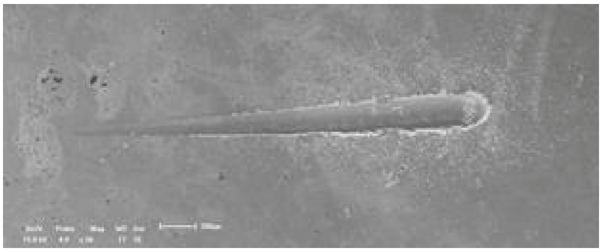


Fig.4 SEM photograph of scratch of DLC thin film

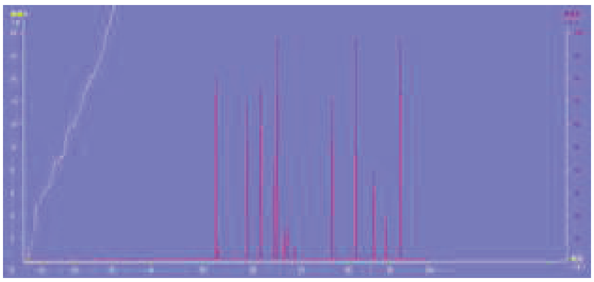


Fig.5 Relationship between load and acoustic emission signal intensity

3.4 Wear-resistance of the DLC thin film

Wear-resistance experiment needs: GCr15 steel ball of φ3.00mm with the hardness of 62HRC. Load: P=2N, rotating rate 1000r/min, grinding crack diameter 6.0 mm. Temperature: 20±2℃, relative humidity: RH＝65％±5％. Sliding time: 10min. observe the grinding crack of DLC thin film and the substrate with optical microscope.

Fig.6 is relationship curve between friction coefficient and friction time of primitive 20CrNiMo samples and DLC thin film. From the figure, it can be known that the average friction coefficient of primitive 20CrNiMo samples is 0.50, while the one of deposited DLC thin film samples is 0.15 under the same conditions. So the latter obviously reduces. This is mainly because the transferring film in the friction procedure of DLC thin film has graphitizing property, thus effectively reducing the friction coefficient.

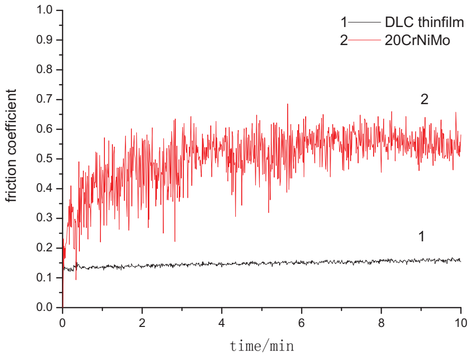
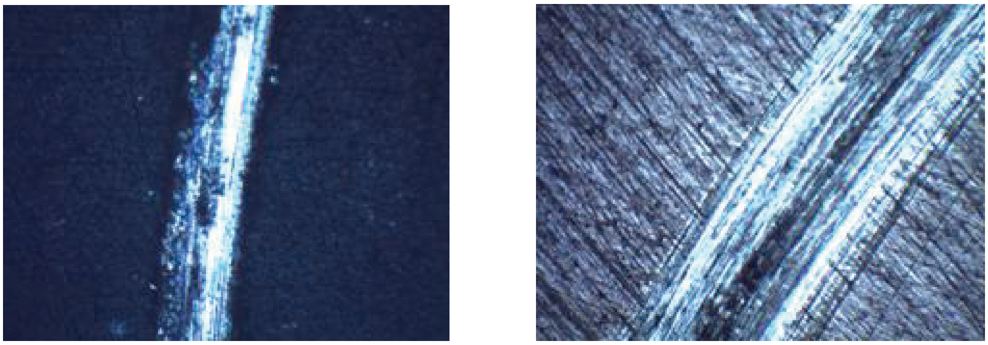


Fig.6 Friction coefficient curve

From the photograph of DLC thin film and 50x optical photograph of primitive 20CrNiMo substrate scratch, we can see the scratch of the deposited DLC thin film samples is even, which belongs to even wearing. In wear experiment, the wearing on the surface of DLC thin film comes from two destroying mechanisms of adherence and friction chemistry. The adhering wear arises from the circumferential force of GCr15 steel ball and DLC thin film during grinding procedure. The loose grains in surface contact area are firstly worn, gradually from soft area to harder area. During the successive grinding procedure, fatigue damage ultimately replaces the migration of single particle, leading to the damage of the film. Adhering wear is related to the hardness of materials, the more the hardness is, the less the wearing is. In addition, there is friction chemistry wear during grinding procedure of DLC thin film, because partial high temperature arises due to friction, diamond of DLC thin film is transferred into graphite, the hardness decreases and the wearing increases. However, the grinding crack of the primitive 20CrNiMo substrate is relatively broad and deep, showing the property of plough. The contrast of grinding crack further demonstrates DLC thin film effectively enhances the wear resistance property of the substrate.



(a) grinding crack of DLC thin film (b) grinding crack of 20CrNiMo substrate

Fig.7 Morphologies of worn surface of DLC thin film and substrate

4. Conclusions

(1) Use hollow-cathode glow discharge method to deposit nonhydrogenous DLC thin film with the depth of 0.6μm on the surface of 20CrNiMo. From Raman spectra, we can know the structure of the prepared DLC thin film not only differs from the lamellar structure of graphite, but also from the tetrahedral structure of diamond, it is a kind of amorphous state (amorphous form) structure.

(2) The prepared DLC thin film is compact and even, with the roughness of 7~8nm. The combination between the thin film and the substrate is close, with the critical load of 52N.

(3) DLC thin film on the surface of 20CrNiMo substrate effectively decreases friction coefficient, enhancing surface wear resistance property.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 50874018).

References

[1]S.S.Camargo, J.R.Gomes, J.M.Carrapichano, et al, Thin Solid Films. 482(2005)221.
[2]M.Vila, J.M.Carrapichano, J.R.Gomes, et al, Wear. 265(2008)940.
[3]Jarratt M, Stallard J, Renevier N M, et al, Diamond and Related Materials. 12(2003)1003.
[4] Yang S, Teer D G, Surface and Coatings Technology. 131(2000)412.
[5] Ikeyama M, Nakao S, Miyagawa Y, et al, Surface and Coatings Technology. 191(2005)38.
[6] Zhao Dongcai, Ren Ni, Ma Zhanji, et al, Chinese Journal of Vacuum Science and Technology. 28(4)(2008)346.
[7]Choy K, Felix E, Mater Sci Eng A. 278(2000)162.
[8]Chunchin Chen, Franklin, Chaunan Hong, Applied Surface Science. 243 (1-4)(2005)296.
[9]Xie Hongmei, Nie Chaoyin, Zhang Biyun, Materials Review. 21(s3)(2007)326.
[10]Zhang Wei, Tanaka Akihiro, Wazumi Koichiro, et al, Diamond and Related Materials.11(2002)1837.
[11]FerrariA C, Robertson J, Phys. Rev. B. 61(2000)14095.
[12]Schwan J , Ulrich S, Roth H, et al, App l. Phys.. 79(1999)1416.
[13]Qu Quanyan, Qiu Wanqi, Zeng Dechang, et al, Chinese Journal of Vacuum Science and Technology. 29(2)(2009)184.